

Heats of Copolymerization of Butadiene and Styrene from Measurements of Heats of Combustion

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The heats of combustion of two samples of polybutadiene and four copolymers of butadiene and styrene prepared at 50° C (122° F), and one sample of polybutadiene and four copolymers polymerized at 5° C (41° F) were measured in a bomb calorimeter. The styrene contents in the copolymers varied from approximately 8 to 55 weight percent.

A value for the heat of polymerization (or copolymerization) was calculated for each sample by combining the experimental value for the heat of combustion with other known thermochemical data. The mean value obtained for the heat of polymerization ($-\Delta H_p^\circ$) of polybutadiene is 17.4 kcal per monomer unit, and the values obtained for the heat of copolymerization varied from 17.1 to 17.7 kcal per monomer unit. No appreciable difference was found between the heats of copolymerization of the 5° C and 50° C polymers. The heat of copolymerization can be represented as a function of styrene content of the polymer by an equation of a form derived theoretically by Alfrey and Lewis, although the conditions under which the polymers were formed were such that some of the assumptions underlying the derivation of the equation were not satisfied.

1. Introduction

Measurements have been made, by means of a bomb calorimeter, of the heats of combustion of three samples of polybutadiene and eight copolymers of butadiene and styrene, ranging in styrene content from approximately 8 to 55 percent by weight (5 to 40 mole %). Two of the samples of polybutadiene and four of the copolymers were prepared by polymerization at 50° C (122° F), whereas the others were polymerized at 5° C (41° F). The data have been combined with other thermochemical data to obtain values for heats of polymerization and copolymerization.

2. Source and Purity of Material

The materials used in this investigation were made available by the Reconstruction Finance Corp., Office of Rubber Reserve, and were purified in the Rubber Section of the Bureau. Some of the properties of the purified materials are given in table 1. The polymers were prepared by emulsion polymerization. The "modifiers" used were commercial *n*-dodecyl mercaptan (DDM) for the 50° C polymers, and commercial tert-dodecyl mercaptan (Sulfole) for the 5° C polymers.

The purification procedure involved dissolving the sample in benzene and precipitating it by pouring the solution slowly into methyl alcohol while stirring. This was done three times. Then the purified sample was again dissolved in benzene, a small amount of phenyl-beta-naphthylamine was added as an antioxidant, the mixture was frozen, and the benzene was removed by sublimation in vacuum to give a product similar to foam rubber in appearance. This procedure removed soap, fatty acid, and stabilizer, as well as some of the low-molecular-weight polymer. In the present work no significant difference was found in the heats of combustion of samples burned as received after the treatment

TABLE 1. Analyses of polymer samples

Polymer	Styrene	Carbon	Hydrogen	Oxygen	Sulfur	Ash	Phenyl-beta-naphthylamine
50° C (122° F) polymers							
	wt %	wt %	wt %	wt %	wt %	wt %	wt % ^a
A-----	0	88.486	11.166	0.145	0.109	0.100	0.00
GL-657----	0	88.656	11.1795	.145	^b .072	.097	.12
GL-658----	8.58	88.907	10.8982	.16	.136	.104	.1
X-452----	23.89	89.42	10.36	.096	.087	.13	.07
GL-662----	42.98	90.100	9.7100	.14	.081	.111	.1
48-B-----	55.73	90.561	9.2643	.15	.046	.158	.07
5° C (41° F) polymers							
B-----	0	88.474	11.1600	0.12	0.083	0.34	0.14
X-454----	8.58	88.869	10.872	.235	^b .056	.18	.13
X-478----	22.61	89.443	10.4008	.15	.048	.098	.11
GL-660----	36.26	89.913	9.9342	.08	.050	.095	.11
GL-661----	53.09	90.513	9.3585	.11	.045	.097	.11

^a Added after analysis.

^b The values reported here are corrected values for sulfur content. For GL-657 the experimentally determined value is 0.150% S and for X-454 0.087% S. See text p. 275.

described above and after further evacuation to about 10⁻⁴ mm of mercury for several days at room temperature.

The purified samples were analyzed quantitatively, and the results are reported in table 1. The styrene contents reported in this table were calculated from the carbon-hydrogen ratios (corrected for mercaptan).

A part of the experimentally determined sulfur content of sample X-454 was found to be present as an inorganic impurity, rather than as mercaptan attached to the polymer chain. The sulfur content reported in table 1 for this sample is the excess of the total observed sulfur over that found to be present in the inorganic impurity. The experimentally determined sulfur content of sample GL-657, which contained no styrene, was higher than that calculated from the observed carbon-hydrogen ratio on the as-

sumption that the sample consisted entirely of dodecyl mercaptan and polybutadiene. It was assumed that the difference was due to sulfur in inorganic impurity (as in the case of sample X-454), and the sulfur content reported is that calculated from the carbon-hydrogen ratio.

3. Method and Apparatus

The apparatus and procedure used in the bomb calorimetric measurements have been described previously [1, 2, 3, 12].¹ The bomb used has a capacity of 381 ml. One milliliter of water was placed in the bomb before each combustion experiment. The polymer samples used were first compressed into pellets.

The calorimetric system was calibrated with NBS Standard Sample 39g of benzoic acid, using the value 26433.8 abs j/g for the heat of combustion of this material under the conditions of the standard bomb process [3, 4, 5].

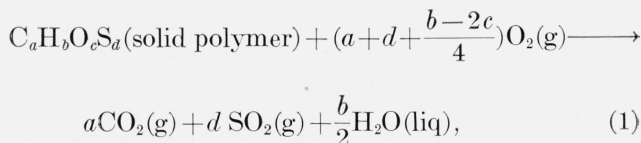
In calculating the results of the heat of combustion measurements, the amount of the combustion reaction in each experiment was determined from the mass of carbon dioxide formed, using the value 44.010 g for the molecular weight of carbon dioxide [21]. Tests were made for carbon monoxide in the gaseous products of combustion after the carbon dioxide had been removed, using a colorimetric method developed at the Bureau [6]. No carbon monoxide was found, and no soot or other evidence of incomplete combustion was found in the bomb in any experiment.

Corrections were applied to the observed heat of combustion in each experiment for heat of stirring, heat transfer between calorimeter and surroundings, ignition energy (22 j), and energy produced by the formation of aqueous nitric (58.8 kJ/mole) and sulfuric (305.7 kJ/mole) acids in the bomb. The last two corrections were made on the basis of the analysis of the washings from the bomb after each combustion experiment. The air initially in the bomb was not flushed out with oxygen in these experiments. The atmospheric nitrogen was left in the bomb because the oxides of nitrogen are known to catalyze the formation of sulfuric acid from sulfur dioxide, oxygen, and water.

The aqueous solution in the bomb at the end of each experiment was analyzed for the acids formed during the combustion by first determining the total acidity of the bomb washings by titration with a standard solution of sodium hydroxide, using methyl orange as the indicator, then removing the nitrate by evaporating the solution to dryness, and finally, determining the sulfur by precipitation as barium sulfate and weighing. The percentage of sulfur so determined averaged 0.01 lower than the values reported in table 1. The total correction for acids did not amount to more than 0.2 percent of the total heat produced in the combustion reaction.

The observed heat of combustion, $-\Delta U_B$, in each experiment was reduced to the value of $-\Delta U_c^\circ$, the

decrease in intrinsic energy accompanying the reaction



using the Washburn procedure [7] modified so as to apply to 28° C and to the energy content of the gases at zero pressure instead of 1 atm.

The measurements were made in terms of the absolute joule as the unit of energy. Conversion to the conventional thermochemical calorie was made by means of the relation

$$1 \text{ cal} = 4.1840 \text{ abs j.}$$

4. Results of the Calibration Experiments

All the measurements of heat of combustion reported in this paper were made with the same calorimetric system. However, the work was carried out over a period of about 2 years, and, because of necessary repairs to the calorimetric system, it was recalibrated several times during the course of the work. Table 2 presents a summary of the values obtained for the energy equivalent of the calorimeter and the numbers of the polymer samples whose heats of combustion were measured, using each value for the energy equivalent.

TABLE 2. Energy equivalent of calorimeter

Energy equivalent	Polymers investigated
$j/^\circ C$	
13784.4±0.7 ^a	A
13972.2±0.8	48-B, X-452, GL-658
13970.2±1.8	GL-657
13964.9±1.8	GL-662
13956.7±1.4	GL-660
	{ GL-661 (experiments 1 and 2)
13956.9±1.4	{ GL-661 (experiments 3 and 4)
13943.4±0.5	X-454
13933.1±1.0	X-478
	B

^a The numbers following the ± signs are the standard deviations of the corresponding mean values of energy equivalent.

5. Experimental Results

The results of the heat of combustion experiments are reported in tables 3 and 4, where $-\Delta U_B$ represents the observed heat of combustion at 28° C under the conditions specified by the volume (381 ml) of the bomb, the mass (1 g) of water placed in the bomb before each experiment, the temperature (28° C) to which the combustion reaction is referred, and the data given in columns 3 and 5; and where $-\Delta U_c^\circ$ represents the decrease in intrinsic energy accompanying reaction (1) with all the reactants and products in their standard thermodynamic states at 28° C. (The data on sample A of 50° C polybutadiene are for 30° C.)

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 3. Results of bomb-calorimetric measurements
50°C polymers

Experiment	Mass of sample	Mass of CO ₂	Initial O ₂ pressure at 28°C	Energy of combustion at 28°C.	
				$-\Delta U_B$	$-\Delta U_c^\circ$
Sample A ^a					
1-----	<i>g</i> 0.90914	<i>g</i> 2.94555	<i>atm</i> 31.9	<i>jjg</i> CO ₂ 13878.2	<i>jjg</i> CO ₂ 13872.8
2-----	.92983	3.01269	31.9	13884.5	13879.2
3-----	.90266	2.92347	32.0	13883.4	13878.0
4-----	.90516	2.93225	32.2	13882.0	13876.6
Mean-----					13876.6
Standard deviation of the mean-----					±1.7
Sample GL-657					
1-----	0.93720	3.04067	31.8	13898.3	13892.6
2-----	.86631	2.81143	32.1	13890.8	13885.2
3-----	.89738	2.91277	32.3	13891.8	13886.1
4-----	.83177	2.70001	32.9	13894.7	13889.0
5-----		2.85568	32.8	13899.5	13893.8
6-----	.89462	2.90321	31.9	13892.8	13887.2
Mean-----					13889.0
Standard deviation of the mean-----					±1.4
Sample GL-658					
1-----	0.92538	3.01453	31.8	13747.3	13741.6
2-----	.89375	2.91014	32.0	13753.4	13747.7
3-----	.90330	2.94091	31.2	13747.1	13741.5
4-----	.88723	2.88905	31.3	13747.3	13741.7
5-----	.85106	2.77228	30.6	13747.2	13741.7
6-----	.88153	2.87141	31.0	13746.3	13740.7
Mean-----					13742.5
Standard deviation of the mean-----					±1.2
Sample X-452					
1-----	1.15567	3.78352	31.4	13498.7	13492.5
2-----	0.95626	3.13200	30.7	13491.9	13486.7
3-----	.78384	2.56602	31.5	13499.7	13494.0
4-----	.80454	2.63482	30.8	13498.2	13492.6
5-----	.89381	2.92658	31.7	13500.6	13494.8
6-----	.88746	2.90639	30.7	13495.3	13489.6
7-----	.85707	2.80670	31.6	13501.1	13495.3
Mean-----					13492.1
Standard deviation of the mean-----					±1.2
Sample GL-662					
1-----	0.94737	3.12610	31.6	13183.4	13177.3
2-----	.94541	3.12019	32.0	13180.1	13173.9
3-----	.96905	3.19821	31.6	13189.0	13182.8
4-----	.85475	2.82085	31.7	13183.8	13177.9
5-----	.89713	2.96068	30.7	13182.3	13176.3
6-----	.89258	2.94579	31.5	13188.2	13182.2
Mean-----					13178.4
Standard deviation of the mean-----					±1.4
Sample 48-B					
1-----	0.92042	3.05117	33.9	12963.7	12957.1
2-----	.91594	3.03606	30.6	12963.9	12957.8
3-----	.94733	3.13950	30.9	12965.5	12959.4
4-----	.93335	3.09382	31.4	12965.4	12959.2
5-----	.96567	3.20112	30.9	12970.3	12964.2
6-----	.94315	3.12581	30.8	12971.1	12965.0
Mean-----					12960.4
Standard deviation of the mean-----					±1.4

^a The data on this sample are for 30° C.

TABLE 4. Results of bomb-calorimetric measurements
5° C polymers

Experiment	Mass of sample	Mass of CO ₂	Initial O ₂ pressure at 28° C	Energy of combustion at 28° C.	
				$-\Delta U_B$	$-\Delta U_c^\circ$
Sample B					
1.....	0.90075	2.91395	30.9	13876.6	13871.1
2.....	.94306	3.04831	31.6	13875.0	13869.3
3.....	.93426	3.02307	31.8	13875.3	13869.6
4.....	.91407	2.95543	31.2	13885.8	13880.2
Mean.....					13872.6
Standard deviation of the mean.....					±2.6
Sample X-454					
1.....	0.90962	2.95790	31.6	13670.5	13664.8
2.....	.91191	2.96572	32.6	13672.7	13666.9
3.....	.89449	2.90938	33.4	13675.1	13669.2
4.....	.90816	2.95355	32.1	13665.1	13659.3
Mean.....					13665.1
Standard deviation of the mean.....					±2.1
Sample X-478					
1.....	0.91363	2.99146	32.0	13508.7	13504.6
2.....	.94549	3.09588	31.6	13502.7	13498.7
3.....	.89638	2.93456	31.9	13498.7	13494.6
4.....	.92084	3.01664	31.2	13501.7	13495.9
Mean.....					13498.4
Standard deviation of the mean.....					±2.2
Sample GL-660					
1.....	0.91793	3.02034	31.9	13287.8	13281.8
2.....	.93561	3.07898	32.1	13289.6	13283.5
3.....	.88791	2.92170	32.0	13283.4	13277.4
4.....	.87460	2.87793	32.0	13284.0	13278.0
5.....	.93032	3.06082	31.9	13292.2	13286.1
Mean.....					13281.4
Standard deviation of the mean.....					±1.7
Sample GL-661					
1.....	0.93293	3.03957	32.7	13015.4	13009.1
2.....	.92041	3.04775	32.6	13011.2	13004.9
3.....	.90656	3.00149	32.6	13015.4	13009.1
4.....	.91953	3.04417	32.9	13023.4	13017.0
Mean.....					13010.0
Standard deviation of the mean.....					±2.6

The values obtained experimentally for the mass of carbon dioxide formed during the combustion are less than those calculated from the carbon content of the samples based on the elemental analysis, the maximum difference being about 0.2 percent. The apparatus for determining the carbon dioxide was tested several times during the course of the work, using NBS Standard Sample 39g of benzoic acid, and was found to give results that check the stoichiometric values within 0.01 percent on the average. The difference between the observed and stoichiometric values for the mass of carbon dioxide formed during the combustion of a polymer is probably due to moisture absorbed by the sample.

The results reported in tables 3 and 4 include the heat of combustion of the phenyl-beta-naphthylamine that was added to the samples as an antioxidant. These results were corrected for the heat

of combustion, $(-\Delta U_c^\circ, 25^\circ \text{C} = 8305.7 \text{ kJ/mole, [9]})$ of this material on the assumption that there was no reaction between the antioxidant and the polymer or air. Table 5 presents these corrected values of $-\Delta U_c^\circ$ and also the corresponding values for $-\Delta H_c^\circ$ (25°C) and ΔH_f° (25°C) used in the calculations of heat of polymerization.

TABLE 5. Corrected values of heat of combustion, and the corresponding values of heat of formation per gram of carbon dioxide formed in combustion

Sample	Butadiene	Styrene	Mercaptan	$-\Delta U_c^\circ$ (28°C)	$-\Delta H_c^\circ$ (25°C)	ΔH_f° (25°C)
50° C polymers						
	Mole%	Mole%	Mole%	j/g CO ₂	j/g CO ₂	j/g CO ₂
A	99.815	0	0.184	13877.9 ± 3.3*	13901.0	73.3
GL-657	99.878	0	.122	13891.5 ± 3.6	13914.6	92.0
GL-658	95.123	4.656	.241	13744.4 ± 3.2	13766.9	78.8
X-452	85.840	13.994	.166	13493.2 ± 3.1	13514.6	87.5
GL-662	71.742	28.085	.173	13179.7 ± 3.6	13200.0	86.5
48-B	60.402	39.492	.107	12961.2 ± 3.1	12980.3	79.3
5° C polymers						
B	99.859	0	0.141	13875.4 ± 4.0	13898.6	74.5
X-454	95.258	4.644	.099	13667.5 ± 3.8	13690.0	13.5
X-478	86.746	13.162	.091	13498.4 ± 3.7	13519.8	77.8
GL-660	77.114	22.784	.103	13283.0 ± 3.5	13302.5	84.6
GL-661	62.916	36.982	.102	13011.3 ± 4.0	13030.4	87.1

* The number following each \pm sign was obtained by appropriately combining the standard deviations of the mean results of calibration and combustion experiments with an estimate (0.005%) of the standard deviation of the value used for the heat of combustion of benzoic acid, and an allowance (0.02%) for systematic errors due to other factors, especially impurities in the samples.

6. Calculation of Heat of Polymerization

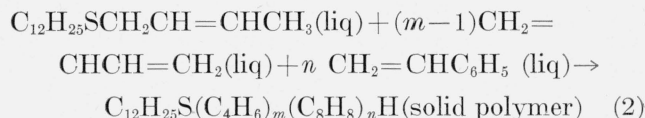
In the case of a polymer such as polystyrene, which consists entirely of styrene units joined together, the heat of polymerization is easily calculated as the difference between heats of combustion per monomer unit of monomer and polymer. A similar calculation could also be made of the heat of copolymerization of two monomers, provided the copolymer contained practically nothing except the two kinds of monomer units. The polymers and copolymers investigated in the present work, however, were prepared by using dodecyl mercaptan as a modifier, so that the calculation of heat of polymerization could not be made by the simple method indicated above.

The calculations made here are based on the chain-transfer theory of polymerization, from which it can be assumed that each polymer molecule contains one dodecyl mercaptan molecule chemically combined with it [10, 11]. In other words, it is assumed that the formula for a polymer molecule can be written $\text{C}_{12}\text{H}_{25}\text{S}(\text{C}_4\text{H}_6)_m(\text{C}_8\text{H}_8)_n\text{H}$, where m and n represent the number of butadiene and styrene units, respectively, in the molecule.² The values of m and n can be calculated from the elemental analysis

² Although this assumption is plausible, and is supported by experimental data [10], it is made here merely as a matter of convenience, in order to simplify the calculation of heats of polymerization. Substantially the same result would be obtained if it were assumed that some of the polymer molecules had mercaptan units at both ends and that the others had hydrogen atoms at both ends.

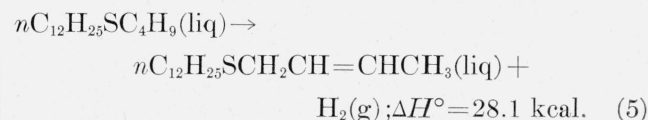
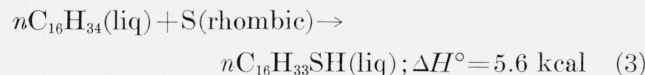
The calculations were actually made on the assumption that a butadiene unit was attached to the mercaptan unit in each molecule. The results would not be changed appreciably by assuming that a styrene unit was attached to the mercaptan.

of the sample. Then the heat of formation of this molecule can be obtained by combining the experimental value for its heat of combustion, according to eq 1 with values for the heats of formation of gaseous carbon dioxide, gaseous sulfur dioxide, and liquid water. The heat, ΔH° , of the reaction



can then be calculated from the heats of formation of the solid polymer and of the reactants. The heat of copolymerization is taken as $(\Delta H_p^\circ = \Delta H^\circ / [(m+n)])$.

Accurate values for the heats of formation of 1,3-butadiene [13, 17] and styrene [18] are available, and are given in table 6. No data on the heat of formation of $\text{C}_{12}\text{H}_{25}\text{SCH}_2\text{CH}=\text{CHCH}_3$ have been found in the literature. Fortunately, only an approximate value is required for the present purpose, and such an approximate value was calculated from other data given in table 6, together with the indicated estimated values for the heats of the following reactions at 25°C :



The value of ΔH° for reaction (3) was taken as equal to the difference between the heats of formation of n -pentane and n -pentanethiol; the value for reaction (4) was taken as the difference between the heats of formation of liquid ethanethiol and liquid dimethylsulphide; the value for reaction (5) was taken as the difference between the heat of formation of liquid n -butane and the mean of the heats of formation of *cis*- and *trans*-2-butene. The values for the heats of formation of the two butenes were obtained from the corresponding values for the ideal gases [13], together with values of heats of vaporization at 25°C to the real gases at saturation pressure [22], that is, the difference in heat content between the real and ideal gases was neglected. The value for the heat of formation of liquid $\text{C}_{12}\text{H}_{25}\text{SCH}_2\text{CH}=\text{CHCH}_3$ obtained in the manner indicated is -72.5 kcal/mole . As suggested previously, and as is evident from the method of calculation, this value can only be regarded as approximate.

Values of heats of polymerization and copolymerization calculated as described above are given in table 7, and are shown plotted against styrene content in figure 1, where the value $-\Delta H_p^\circ = 16.68 \text{ kcal per monomer unit for styrene}$ [12] is also shown.

TABLE 6. Values of heats of formation at 25° C used in calculating heats of polymerization

Compound	ΔH_f°	Reference
	kcal/mole	
<i>n</i> -Pentane (liq).....	-41.36	[14]
<i>n</i> -Pentanethiol (liq).....	-35.8	[15]
Ethanethiol (liq).....	-16	[16]
Dimethylsulfide (liq).....	-13.6	[16]
<i>n</i> -Butane (liq).....	-35.51	[13, 14]
2-Butene (liq).....	^a -7.43	[13, 22]
1,3-Butadiene (liq).....	+20.88	[13, 17]
Styrene (liq).....	+24.83	[18]
<i>n</i> -Hexadecane (liq).....	-108.59	[14]

^a Mean of values for *cis* and *trans* isomers.

TABLE 7. Heats of polymerization

Sample	Styrene content	$-\Delta H_p^\circ$ (25° C)
50° C polymers		
	Mole % ^a	kcal/monomer unit
A.....	0	17.6
GL-657.....	0	16.9
GL-658.....	4.65	17.4
X-452.....	14.02	17.1
GL-662.....	28.13	17.2
48-B.....	39.53	17.7
Polystyrene.....	100	^b 16.7
5° C polymers		
B.....	0	17.6
X-454.....	4.65	20.4
X-478.....	13.17	17.6
GL-660.....	22.84	17.3
GL-661.....	37.02	17.2

^a Mole percent styrene plus mole percent butadiene=100.

^b Roberts, Walton, and Jessup [12]. This sample contained no sulfur, and the heat of polymerization was calculated as the difference between the heat of combustion per monomer-unit of polymer and monomer.

7. Discussion

It is apparent from figure 1 that the value 20.4 kcal per monomer unit for $-\Delta H_p^\circ$ for the 5° C polymer X-454 is entirely out of line with the values for the other polymers, which range from 16.9 to 17.7 kcal per monomer unit. No satisfactory explanation of this high value has been found, but the reasonably good consistency of the data on the other polymers suggests that the high value of $-\Delta H_p^\circ$ for sample X-454 may be related to some abnormality in the composition of this sample. Some abnormality in this sample is also indicated by a correlation of the refractive indices of the various polymers with styrene content [20]. It has been found that the styrene contents of the other 5° C polymers, as determined from analyses for carbon, hydrogen, and sulfur, can be represented by an empirical function of refractive index within a few thousandths of 1 percent of styrene. However, this relation gives a value for styrene content for sample X-454 that is lower than the value calculated from the analysis of the sample by approximately 0.5 percent.

As stated previously, a part of the sulfur in sample X-454 was present as inorganic impurity, and it may be that the inorganic sulfur compound took

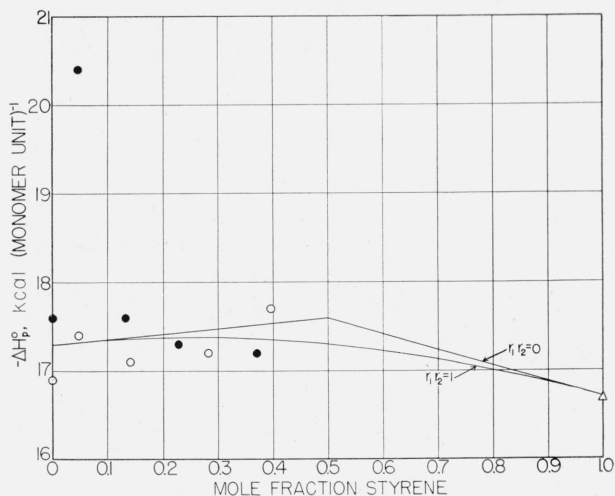


FIGURE 1. Heats of copolymerization.

○, 50° C polymers; ●, 5° C polymers; △, polystyrene.

part in some reaction in the bomb. Since the nature of the sulfur compound is not known, no correction for the effect of such reactions could be made. Calculated values of the correction on the basis of various assumptions as to what sulfur compounds may have been present and what reactions may have taken place indicate that the error introduced by neglecting the thermal effect of the reaction, and by making corrections for nitric and sulfuric acids as described previously, probably does not exceed 0.02 or 0.03 percent of the heat of combustion. This is far too small to account for the abnormal result obtained with sample X-454.

It will be seen from figure 1 that the values of $-\Delta H_p^\circ$ for samples other than X-454 do not indicate any appreciable difference between the 5° C and the 50° C polymers. It will be seen also that the points for polymers other than X-454 lie reasonably near to the curves shown. The maximum deviation from either curve corresponds to about 0.06 percent in heat of combustion of the polymer. This is probably as good agreement as could be expected, considering the nature of the polymeric materials and the approximations made in calculating the heats of polymerization.

The curves shown in figure 1 were calculated from an equation of a form derived theoretically by Alfrey and Lewis [19], which expresses heat of copolymerization as a function of copolymer composition. A value for one of the two parameters in this equation was chosen empirically to fit the experimental data. According to Alfrey and Lewis [19] the other parameter, designated as $r_1 r_2$, was less than or equal to unity in all copolymer pairs studied by them. The two curves shown in figure 1 may therefore represent the limits between which the best theoretical curve would lie. It is seen from figure 1 that the data are at least not inconsistent with the theoretical curves. It may be noted also that the deviation of the curves from a straight line connecting the values for 0 and 100 percent of

styrene is in the direction predicted by Alfrey and Lewis. It should be pointed out, however, that the polymers investigated here were prepared under conditions such that conversion ranged from 60 to 75 percent, whereas Alfrey and Lewis [19] state that their analysis applies only for low-conversion polymerization, without appreciable drift in monomer ratio.

It seems unlikely from the information available on the polymers investigated and from the results of infrared studies on similar polymers by Hart and Meyer [8] that any appreciable differences in heat of polymerization would arise from differences in the relative amounts of 1,2 and *cis*- and *trans*-1,4 structures in various polymer samples.

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